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A MODIFIED LANGMUIR EQUATION FOR PREDICTING SORPTION OF METHYLACRIDINIUM ION IN SOILS AND SEDIMENTS

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A Modified Langmuir Equation for Predicting Sorption of Methylacridinium Ion in Soils and Sediments[1]

DAVID S. BROWN AND GEORGE COMBS[2]

ABSTRACT

An empirical model for predicting sorption isotherms of organic cations was tested using a set of 10 soils and sediments. The model is based on a competitive Langmuir equation with modifications for grouping the various competing ion species and for normalizing over a broad range of sediment properties. Normalization is accomplished by substituting cation exchange capacities (CECs) determined with NH_4^+ for the Langmuir capacity term. Natural exchange ions are grouped and treated as a single competing species for simplicity. A single calibration enables estimation of sorption isotherms for other sediments for which estimates of CECs and competing electrolyte concentrations are known.

Additional Index Words: **cation exchange, pollutant sorption, competitive Langmuir equation.**

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The need to predict the transport of toxic chemicals in air, water, and soil/sediment systems has generated considerable interest in the development of environmental models as convenient tools. Basic to constructing such models is the ability to predict rates and magnitudes of the individual transport and transformation processes. Sorption; volatilization; and chemical, biological, and photochemical degradation data are typical input requirements. Sorption processes play a key role because these equilibria often determine the solution concentrations that drive the other attenuation processes in sediment-water systems.

During the past several years, significant progress has been made in predicting partition coefficients for neutral, hydrophobic compounds in natural sediments. Contributions from Lambert (9, 10), Hance (6), Briggs (2), Karickhoff et al. (8), Hassett et al. (7), and others have resulted in a useful system for predicting sorption for a broad range of hydrophobic compounds. Equations developed from these efforts enable calculation of sorption coefficients from the organic C content of the sorbent and either the octanol/water partition coefficient or the water solubility of the sorbate. Estimates of this kind can be useful for environmental transport models. Unfortunately, predictive equations of this type are not available for estimating ionic sorption.

The multicomponent nature of soil and sediment systems gives rise to several difficulties in making quantitative predictions of cation exchange. The suite of natural ions varies both in character (species distribution) and in concentration with individual sediments. Competitive interactions of these and other ions of interest with the exchanger must be addressed. Despite the long history of work in cation exchange (12, 13), few attempts have been made to quantitatively evaluate exchange systems involving more than two competing ions. Elprince and Babcock (3) used the Wilson (15) equation to construct three-component exchange isotherms for monovalent ion groups on clay minerals. Wiedenfield and Hossner (14) used a similar approach in a soil system with the heterovalent Ca^{2+}, Mg^{2+}, and Na^+ ion suite. These investigators used experimental inputs from binary systems and did not provide actual data on ternary ion systems for comparison. Elprince et al. (4) made this comparison in a montmorillonite system with the NH_4^+, Ba^{2+}, La^{3+} ion group. Calculations based on binary exchange pairs were in reasonable agreement with data collected in the simultaneous three-cation exchange system even though the model did not provide good fits for two of the three binary pairs.

Unfortunately, these methods have apparently not been extended to whole soils and sediments or to systems containing more than three ion species. To do so would complicate the calculations and limit their utility in many environmental assessment applications. Indeed, the measurements necessary for establishing the input parameters for a given site would probably be more laborious than determining the system composition directly. Thus, a more utilitarian, and admittedly less elegant, approach would be advantageous. It was toward this end that the present work was directed. The goal was to test a simple model for estimating sorption of organic cations in natural soils and sediments. The starting point was a competitive Langmuir-type model as developed and used by Boyd et al. (1) in well-defined sorbent systems. The objective was to modify the model to facilitate simple normalization of sediment properties and test the applicability of the normalized equation in a vareity of natural sorbents.

Methylacridinium ion, hereafter referred to as MAC^+, was selected as the test ion. It is reasonably stable, easily quantified spectroscopically, and has no interfering pK equilibria. The use of MAC^+ also eliminated the need to distinguish natural from added test ion concentrations since it was not initially present in any of the natural sorbent systems.

MATERIALS AND METHODS[3]

SEDIMENT PREPARATION

Ten test soils and sediments were obtained (from Dr. J. J. Hassett, Univ. of Illinois, Urbana) and were used without further preparation. All sediments were from a larger collection used in several previous studies. Sample collection and characterization procedures were described in detail by Hassett et al. (7). A summary of important sediment characteristics is given in Table 1.

COMPOUND PREPARATION

Methylacridinium chloride was prepared by methylation of acridine with dimethyl sulfate in nitrobenzene at 160°C. The resulting solution

[1] Contribution of the Environ. Res. Lab., USEPA, Athens, GA 30613. Received 30 Mar. 1984.

[2] Research soil scientist and physical science aide, respectively, USEPA.

[3] Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the USEPA.

Table 1. Characteristics of soils and sediments investigated.†

Sample	Location	O.C.	CEC	Clay
		g kg^{-1}	cmol (i) kg^{-1}	g kg^{-1}
EPA-3	North Dakota	15.3	12.7	241
EPA-14	West Virginia	4.8	18.9	636
EPA-15	Ohio River	9.5	11.3	357
EPA-16	Indiana	12.0	10.5	390
EPA-19	Kentucky	17.7	7.64	251
EPA-20	Illinois	13.0	8.50	286
EPA-23	Sangamon River	23.8	31.2	691
EPA-24	Illinois	9.5	6.28	208
EPA-B1	Georgia	9.0	3.00	225
EPA-B2	Oconee River	12.1	3.72	186

† Supplied by J. J. Hassett, Univ. of Illinois, Urbana.

was cooled to room temperature and poured into ether, then filtered to collect the precipitated acridinium methosulfate. Conversion to the chloride was accomplished by saturating a boiling, concentrated aqueous solution of the methosulfate with NaCl. Purity was checked by comparing the nuclear magnetic response (NMR) and ultraviolet (UV) spectra with reference data. No discrepancies were observed.

ADSORPTION ISOTHERMS

Adsorption isotherms were determined by adding varying quantities of MAC$^+$ to sediment and water mixtures containing 1.0 g of sediment and 40 mL of solution. The sediment concentrations were 25 g L^{-1} in all systems. To obtain equilibrium, samples were agitated gently on an orbital shaker overnight at 25°C. Phase separations were accomplished by centrifugation at 27 000 × *g* (15 000 rpm) for 1 h using closed stainless steel tubes in a Sorvall® RC2-B centrifuge equipped with an SS-34 rotor. Aliquots of the equilibrium supernatants were collected for direct analysis for MAC$^+$ using either a Perkin Elmer® 356 or a Cary® 219 spectrophotometer. In either case, blank samples containing only water and sediment were carried through the procedure for use as reference samples in the analysis. Each isotherm was determined through measurements of eight different MAC$^+$ concentrations along the curve.

Mass balance checks for MAC$^+$ in the sediment phase were carried out on a few samples by converting the cation to the neutral acridone followed by extraction with methylene chloride and absorption analysis. The conversion was accomplished by adding 0.15*M* NaOH to form the neutral 9-hydroxy-*N*-methylacridium analog and oxidizing it to the acridone by bubbling air through the solution. Recoveries averaged 86%.

Separate aliquots of the equilibrium supernatants were collected for inorganic ion analysis by plasma emission techniques. These analyses were performed on the fresh, untreated supernatants by the Georgia State Soil Test Laboratory (Athens, GA) using their standard spectrometric method. Metals measured included K, Ca, Mg, Mn, Fe, Al, Cu, Zn, Na, Pb, Cd, Ni, Cr, and Mo. If concentrations for individual metals were < 0.01 mg L^{-1}, the results had negligible effect on the isotherm calculations and were dropped.

Additional metal analyses were performed on a few of the sediments as a quality control check. These analysis were performed on fresh samples using an Applied Research Laboratories® ICP-QA 137 inductively coupled plasma atomic emission spectrometer. Equilibrium supernatants from the isotherms were used without further processing. These determinations included Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Te, Th, Ti, Tl, V, Y, and Zn. The independent analyses compared well in all cases where direct comparisons were possible. Sodium and K lines were not available on the in-house instrument for comparison.

For isotherm calculations it was necessary to assign valence states to the elements present at high enough concentrations (> 0.01 mg L^{-1}) to be used in the model. The group of elements meeting this criteria included Ca, Mg, Na, K, Al, Fe, and Mn. Within this group, Fe and Al were treated as trivalent; Ca, Mg, and Mn as divalent; and Na and K as monovalent. No attempt was made to account for speciation of Fe and Al because the laboratory measurements were for total metal only.

Hydronium ion concentrations were determined by calculation rather than direct measurement. This was accomplished by assuming hydronium ion expelled from the exchanger equalled the difference between MAC$^+$ sorbed and the summed measured concentrations of the expelled ions. This method assumes constant charge balance on the sediments, but avoids problems in trying to make very high-precision pH measurements and accounting for side reactions involving the hydronium ion (H_3O^+).

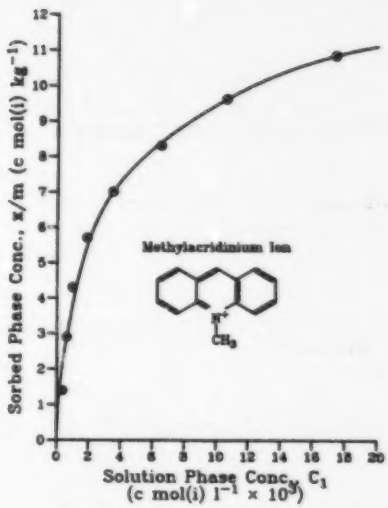

Fig. 1. Example sorption isotherm for MAC$^+$ on sediment EPA-3.

RESULTS AND DISCUSSION

An example isotherm is shown in Fig. 1 for MAC$^+$ on sediment no. 3. The nonlinear behavior illustrated was typical for all the sediments, although they varied considerably in range of concentrations where noticeable curvature began to occur, or where the plateau was beginning. This was to be expected from the wide range of sediment characteristics represented (Table 1). In addition, competing electrolytes varied substantially among the sediments. The intercept in Fig. 2 illustrates the background concentration of cations in sediment no. 3 without additions of MAC$^+$. The linear increase in equilibrium solution ion concentration as metals were displaced from the sediments by increasing MAC$^+$ additions is also shown. This is illustrated individually for the four predominant competing ions (Ca^{2+}, Mg^{2+}, Na^+, K^+) and for the sum of the expelled ions measured. Hydronium ion contributions were not included in the total shown in Fig. 2.

Solution concentrations of other ions in the group measured increased linearly with MAC$^+$ sorption but were present in lower concentrations and had little influence on the sorption equilibrium. Calcium, Mg, Na, and K ions were the predominant competitors in most of the other sediments as well. In some sediments Al^{3+}, Fe^{3+}, or Mn^{2+} made substantial contributions. Hydronium ion contributions were also important in most cases. These were calculated rather than measured. Because of the logarithmic relationship between pH and H_3O^+ concentration the precision in measuring small changes in hydronium ion concentrations is a function of pH. In many of the sediments this limitation precluded direct measurement of hydronium ion concentrations with enough precision to be of use in calibrating

the model. Competing equilibria involving hydronium ion would have given rise to interpretation difficulties even if direct measurement had been possible. Because of this hydronium ion, concentration changes along the isotherm were determined by difference, assuming constant charge balance on the exchanger. Hydronium ion expelled from the sediment was equated to the difference between MAC^+ sorbed and the sum of other measured expelled ions. Hydronium ion contributions determined in this way typically accounted for about one-third of the displaced ion suite. Figure 3 illustrates this for sediment no. 3. In this case, the measured total of displaced ions accounted for 76% of the MAC^+ sorbed. The remaining 24% was assigned to hydronium ion. Considering all sediments in the set, this correction ranged from 6 to 72% depending on pH and inherent natural electrolyte concentrations. The mean correction was 33%, due to H_3O^+.

Figure 3 also illustrates the linear correspondence between reductions in MAC^+ equilibrium solution concentrations and increases in the summed competing ion concentrations due to exchange. The absence of an intercept in Fig. 3 is justification for dropping ions present at levels < 0.01 mg L^{-1}. All sediments investigated behaved similar to sediment no. 3 with respect to competitive exchange. Linear relationships like that illustrated in Fig. 3 were obtained.

Boyd et al. (1) evaluated competitive exchange of various cations in organic zeolites. Behavior of their systems was adequately treated using a competitive exchange equation fashioned by formal analogy to the Langmuir equation for sorption from a binary gaseous mixture

$$x/m = (K\, b_1\, C_1)/(1 + b_1C_1 + b_2C_2) \qquad [1]$$

in which x/m is the amount of ion 1 sorbed per unit weight of adsorbent and C_1 and C_2 are the respective solution concentrations of ions 1 and 2. Relative preference of ions 1 and 2 for the sorbent are expressed by the constants b_1 and b_2; while K is a constant representing the sorption capacity of the solid phase. Systems containing more than two competing ion species could be represented similarily by an equation of the form

$$x/m = (K\, b_1\, C_1)/(1 + \sum_{i=1}^{n} b_iC_i) \qquad [2]$$

although evaluation of the constants would be difficult for complex systems.

In many systems where $b_1C_1 + b_2C_2 \gg 1$, Eq. [1] can be reduced to the linear form

$$(C_1/C_2)/(x/m) = b_2/b_1K + C_1/C_2K \qquad [3]$$

which facilitates graphical evaluation of the constants. Sposito (11) developed this kind of relationship using statistical mechanics.

The utility of these competitive equations in normalizing nonlinear effects due to varying sorbent concentrations and sorption loading levels was demonstrated by Griffin and Au (5). Representing their binary Pb/Camontmorillonite exchange isotherms with the simple Langmuir equation resulted in different isotherms as a

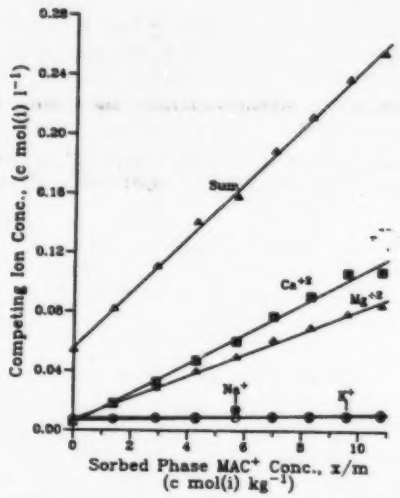

Fig. 2. Concentrations of competing exchange ions in equilibrium solution as a function of sorbed concentrations of added MAC^+.

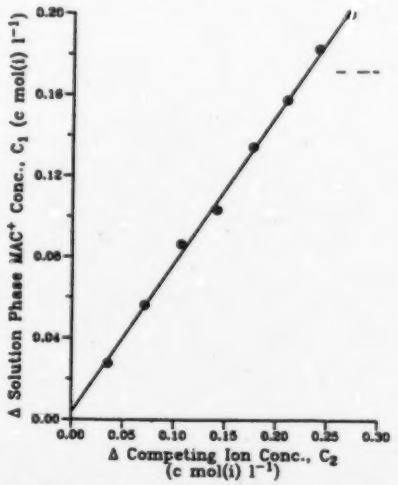

Fig. 3. Relationship between changes in solution concentrations of MAC^+ (C_1) before and after sorption and the corresponding change in the summed concentrations of competing ions (C_2).

function of clay concentration. Use of the competitive equation resolved all the isotherms to a single linear adsorption plot of the form given by Eq. [3].

Unfortunately, the simple graphical determination of constants available from Eq. [3] was not applicable to the diverse set of natural sediments investigated in this work. Strictly speaking, Eq. [3] is only useful in treating simple competitive exchange between a single pair of ions. For complex natural systems containing many competing species, an expansion of the form of Eq. [2] would be more appropriate. Even then, no allowance is made for the possibility of heterovalent exchange. In any case, expansion of Eq. [2] to a large number of terms would complicate the evaluation of constants to the point of impracticality. Precise fitting of several constants would require a large, high quality data set.

In this work, several assumptions were employed for simplification. First, a simple binary model of the form

in Eq. [1] was chosen as a starting point. This embodied the assumption that the suite of ions originally present in the sediments could be summed and treated as a single competing species. Thus, the competing ion concentration C_2 in Eq. [1] is given by

$$C_2 = \sum_{i=2}^{n} C_i \qquad [4]$$

where n is the number of natural ion species to be treated. Ion species present at concentrations < 0.01 mg L^{-1} were not included in the isotherm calculations.

There are two sources of error in grouping all competing ion species into a single term. The valences are not equal and concentration terms do not add linearly. Also, relative preferences of the various species for the exchanger are not equal. Hence, the group of competing ion species cannot be correctly represented by a single constant (b_2). Nevertheless, both these approximations are justifiable because the group of ions represented by C_2 is dominated by Ca^{2+} in the majority of soils and sediments. From this perspective, C_2 is composed of a single dominant term in which both valence and exchange preference are clearly defined. One could represent isotherms for many sediments reasonably well by considering only Ca^{2+} as a competitor. Magnesium would often be a second important competitor and would behave similarly to Ca^{2+}. This is especially true in cases where the competition is with a strongly sorbed organic ion such as MAC^+ where the ratio b_1/b_2 is 100 or more. In these cases, the denominator of Eq. [2] is dominated by the product b_1C_1, even at relatively low values of C_1.

As a further simplification, and to eliminate some of the problems with fitting multiple parameters, the capacity term (K) from Eq. [1] was replaced by standard cation exchange capacities (CEC) as measured with NH_4^+. Figure 4 illustrated the correspondence between estimated K values determined from MAC^+ isotherms for individual sediments and NH_4^+ CECs as determined by Hassett et al. (7). Values of K were obtained from the slopes of plots of $C_1/C_2/x/m$ vs. C_1/C_2. In some cases, the assumption ($b_1C_1 + b_2C_2 \gg 1$) used in arriving at Eq. [3] was not met and the data deviated from the line at low ratios of C_1/C_2. When this happened, the lower points were overlooked and slopes were taken from the linear part of the plot. The line shown in Fig. 4 is the line of zero difference between K and CEC. Some scatter is apparent. The greatest deviations are for the two highest points representing CECs of 18.9 and 31.2 cmol (i) kg^{-1}. In both cases, K was less than expected from the CEC. The possibility of steric hindrance at high loading levels is great for a sorbate as large as MAC^+. For this reason, statistical tests were based on the remaining points in Fig. 4. Linear regression analysis gave a slope of 0.95 and intercept of 0.52. Additional tests indicated the slope was not significantly different from 1.0 and the intercept was not significantly different from zero. A direct substitution of CEC for K was used in the equations. This was especially advantageous from the modeling standpoint because standard CEC values are widely catelogued in the literature. Caution should be used in making this

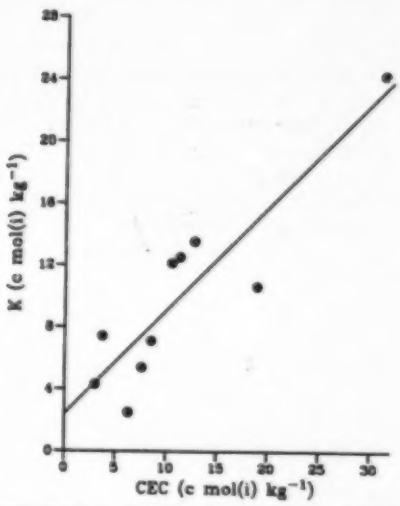

Fig. 4. Correspondence of Langmuir capacity term (K) from sorption isotherms to CEC. The line shown is the line of zero difference.

substitution for high CEC sediments if the sorbate molecule is large.

With the CEC substitution in place, the grouped-ion competitive model was tested in the form

$$x/m = (\text{CEC}\, b_1C_1)/(1 + b_1C_1) + b_2 \sum_{i=2}^{n} C_i) \qquad [5]$$

where b_1 and b_2 are constants reflecting relative preferences for the MAC^+ test ion and the grouped competing ion suite, respectively. Trial and error methods were used to determine a single set of values for b_1 and b_2 for the ten test sediments. This resulted in values of $b_1 = 50$ and $b_2 = 0.5$ when the solid phase concentration of MAC^+ (x/m) was expressed in units of mmol (i) kg^{-1} and solution concentrations in mmol (i) L^{-1}. The procedure for estimating b_1 and b_2 began by calculating the products b_1C_1 and $b_2 \Sigma_{i=2}^{n} C_i$ for all data points. Initial estimates of b_1 were obtained from points that best isolated the influence of b_1C_1 in the denominator of Eq. [5]. These were cases where b_1C_1 was larger than the other terms in the denominator. Likewise, an initial estimate of b_2 was calculated by selecting a point where the b_2 term had a predominant influence. The initial estimate of b_1 was substituted into the equation along with the CEC and measured values of C_1 and $\Sigma_{i=2}^{n} C_i$ to calculate an initial b_2 value.

Initial estimates of b_1 and b_2 were used to calculate x/m for comparison with measured values of x/m for all sediments at various MAC^+ concentrations. This process was repeated several times while making small adjustments in b_1 or b_2 until no further improvement in fit (determined by inspection) was obtained. Adjustments in b_1 and b_2 were made in increments of 1.0 and 0.1, respectively. This method was supplemented by some experimental spot checks using sediment 14 as a test case. To better isolate the effects of b_1 and b_2, artificial systems were prepared that exaggerated the range of background electrolyte concentrations available from the untreated sediments. This was accomplished by leaching one portion of sediment 14 with water to

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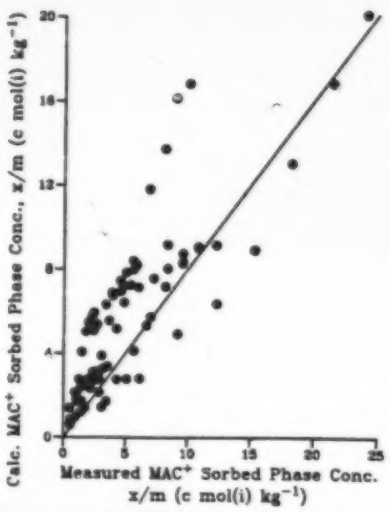

Fig. 5. Comparison of calculated and measured concentrations of MAC^+ on all sediments.

remove excess free electrolytes and adding high $CaCl_2$ concentrations to another in an attempt to make $\Sigma_{i=2}^{n} C_i$ virtually constant. Isotherms run on these systems reflected extremes in influence of the b_2 term in Eq. [5]. Final $\Sigma_{i=2}^{n} C_i$ concentrations were more than three orders of magnitude different in the two cases. Results were compatible with the trial and error estimates of the coefficients.

The final set of predicted vs. measured values of x/m are compared in Fig. 5. Included in the plot are points representing various concentrations of added MAC^+ for each of the test sediments. The line of unit slope is shown for reference. Substantial scatter is apparent. Regression analysis gave an estimated slope and intercept of 0.723 and 1.94, respectively, with a r^2 value of 0.690. The estimated slope was significantly different from 1.0 and the intercept was significantly different from zero, both at the 0.0001 level. This indicated some bias; a possible result of imperfections in determining calibration parameters incrementally as well as overlooking obvious errors in treating the grouped ions with only one preference constant (b_2). Most points are within a factor of two of the measured values, however. Often the input concentrations for a model of this type would not be known more precisely than a factor of two. As such, the utility of developing more elegant and complex models is limited to situations where high quality input data are available.

SUMMARY

Several approximations were employed in developing a utilitarian, empirical cation exchange model. The key factor in normalizing sediment characteristics was the substitution of CEC for the Langmuir capacity term K. This enables one to extrapolate to new sediments with knowledge of the appropriate CECs. Background information on competing ion concentrations would also be required. This constraint was minimized by grouping all competing ion species into a single term to minimize difficulties in estimating model parameters. The competing ion suite was primarily composed of Ca^{2+}, Mg^{2+}, Na^+, and K^+. Within this group, Ca^{2+} was often dominant. Reasonable estimates of background concentrations for these ions are available from water quality studies in many local modeling situations. Use of the model for new pollutant ions would require calibration of ion preference parameters b_1 and b_2. The sensitivity of quantitative predictions to errors in estimating b_1 and b_2 is a function of their relative magnitudes as well as the respective ion concentrations. In situations where either b_1C_1 or b_2C_2 dominate the denominator of Eq. [1], competitive effects are lost and Eq. [1] effectively reverts to the conventional Langmuir form.

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